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STRUCTURE AND PROPERTIES OF GLASS CERAMICS AFTER LASER TREATMENT

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Experimental results of the study of the laser radiation effect on glass ceramic cement and photosensitive glass ceramics are discussed. Laser beam treatment renders the structure amorphous and facilitates the emergence of microcracks and modification of the mechanical and dielectric properties of the materials.

Laser technologies in the last years have gained wide acceptance in production of articles made of glass ceramic materials [1].

To determine the expediency of using a laser to solve a specific technological task, it is necessary to understand well the mechanism of interaction of laser radiation with the material and the possibilities of using existing lasers.

The authors investigated the mechanism of interaction of laser radiation with glass ceramic cement (a glass ceramic material commonly used in the production of gas-discharge indicators) [2]. The considered glass ceramic cement samples were subjected to different heat treatment procedures. The samples were irradiated with an LGI-37-2-01 laser with a radiation pulse of 0.5 ms and wavelength 500 Å. The radiation flux density was calculated by the formula

$$q = 4P/(\pi d^2), \qquad (1)$$

where P is the laser radiation power; d is the focus spot diameter.

It amounted to 1.6×10^2 W/cm^2. The radiation was focused using a standard optical lens with a focus distance of 15 cm.

The analysis revealed the phase composition of the radiated and non-radiated samples to be identical, except for a slight difference observed in the non-radiated samples crystallized at temperature 530°C and higher. The following crystal phases were identified in the mentioned samples: $ZrSiO_4$, $2PbO \cdot Ba_2O_3 \cdot ZnO$, α-$PbO \cdot Ba_2O_3$; in the samples exposed to laser radiation and the same crystallization procedure, the α-$PbO \cdot Ba_2O_3$ phase is absent. The x-ray phase analysis revealed a substantial difference in the content of the crystalline phase of the radiated and non-radiated samples (Table 1, Figs. 1 and 2).

The obtained experimental data show that the effect of laser radiation on glass ceramic cement regularly decreases the crystal phase content. Thus, the content of the crystal

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TABLE 1

Treatment temperature, °C	Volume content of the crystal phase, %		Microhardness, GPa	
	before radiation	after radiation	before radiation	after radiation
390	5	9	1.74	2.10
400	10	6	1.03	2.79
410	8	11	–	–
420	35	22	1.41	–
430	58	10	2.02	4.61
440	54	21	3.70	–
450	62	32	3.86	2.02
460	60	29	5.15	2.71
470	61	41	3.53	2.27
480	55	27	4.62	3.94
490	58	31	3.74	2.67
500	63	55	4.68	2.83
510	70	29	3.34	–
520	37	23	–	2.24
530	40	23	4.86	–
540	55	31	3.97	3.12
550	23	16	3.92	–
560	33	27	4.06	3.63
580	25	20	–	–

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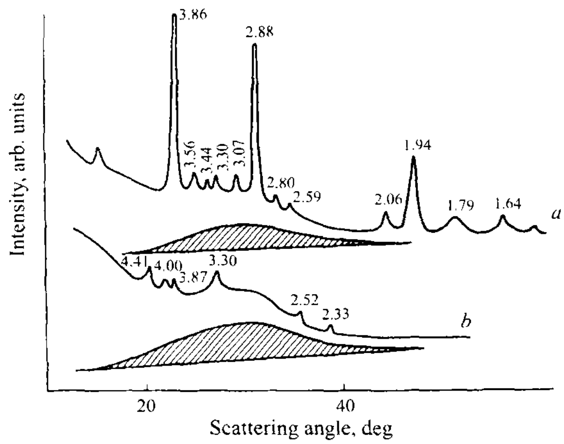

Fig. 1. Diffraction pattern of glass ceramic cement heat-treated at temperature 430°C: *a*) before radiation; *b*) after radiation.

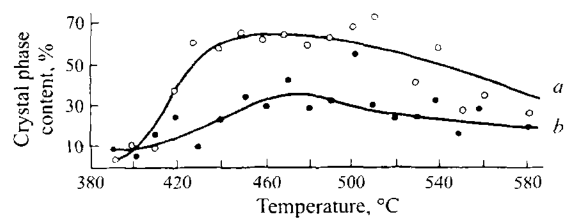

Fig. 2. Content of the crystal phase in heat-treated glass ceramic cements versus crystallization temperature: *a*) before radiation; *b*) after radiation.

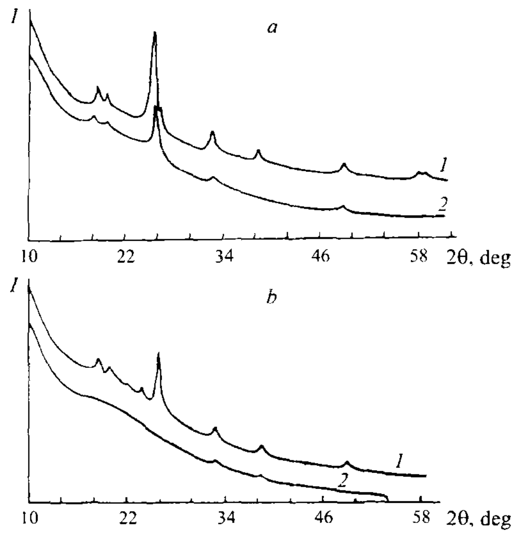

Fig. 3. Diffraction patterns of photoglass ceramic samples after heat treatment at temperatures 780°C (*1*) and 585°C (*2*) before (*a*) and after (*b*) laser radiation.

phase in the non-radiated samples crystallized at temperatures 420, 430, 440, 450, and 460°C amounted to 35, 58, 54, 62, and 60%, respectively, and the same parameter in the samples after laser treatment was 22, 10, 21, 32, and 29%.

The diffraction patterns of glass ceramic cement samples irradiated by laser exhibit a decreased intensity of the crystal phase reflections and an increase in the amorphous halo intensity (Fig. 1). It should be noted that laser radiation produces considerable modifications of the mechanical properties of glass ceramic cements (Table 1). Thus, the microhardness of the initial samples crystallized at temperatures 440, 450, 460, and 470°C attained 3.70, 3.86, 5.15, 3.53 GPa, respectively, and in the radiated samples it was only 2.02, 2.71 GPa.

Analysis of the obtained experimental data points to a complex dependence of the crystal phase content, microstructure, and mechanical properties of glass ceramics on laser radiation. Millisecond pulses cause a high rate of heating of the material, which results in the crystal phase melting, a decrease in the crystal sizes, and an increase in the amorphous phase content in the samples. Visual inspection of the radiated sample surface revealed the appearance of caverns attesting to the evaporation and release of the material. Thus, laser radiation significantly modifies the structure and composition of the surface layer of the material.

In order to study the laser beam effect on lithium-aluminosilicate photo-sensitive glass ceramic, photosensitive glass of the following chemical composition was synthesized (wt.%: 73.0 SiO_2, 8.0 Al_2O_3, 13.0 Li_2O, 2.0 ZnO, 4.0 K_2O) to which 0.04 wt.% $AgNO_3$ was additionally introduced. The samples shaped as flat plates 50 mm in diameter and 2 mm thick were irradiated by ultraviolet light for 30 min and then heat-treated at temperatures 520, 585, and 780°C [3]. The laser treatment of the photoglass ceramics was performed on an LG-43 unit using continuous radiation from a CO_2-laser with wavelength 10.6×10^4 Å which was focused by a NaCl lens with focus distance 10 cm. The focus spot diameter was to 0.5 mm. The radiating power determined by a IMO-2 medium-power meter was equal to 25 W. The power flux density calculated according to Eq. (1) amounted to 10^4 W/cm^2 with a pump voltage of 2 kW and a working current of 30 mA. The diffraction patterns of the photo glass ceramics before and after laser treatment are shown in Fig. 3.

X-ray phase analysis established that the samples not treated by the laser beam are amorphous both before and after heat treatment at 520°C. The samples heat-treated at temperature 585°C exhibited crystal phases of lithium metasilicate $Li_2O \cdot SiO_2$ and a solid solution of β-eucryptite $Li_2O \cdot Al_2O_3 \cdot 2SiO_2$ and after heat treatment at 780°C it exhibited an additional crystal phase: lithium disilicate $Li_2O \cdot 2SiO_2$.

Laser-beam treatment produces changes in the quantitative and qualitative phase composition of the photoglass ceramic. The crystal phases based on lithium metasilicate and β-eucryptite in the sample heat-treated at temperature 585°C melted. The surface layer is rendered amorphous and the nature of the x-ray scattering corresponds to the amorphous

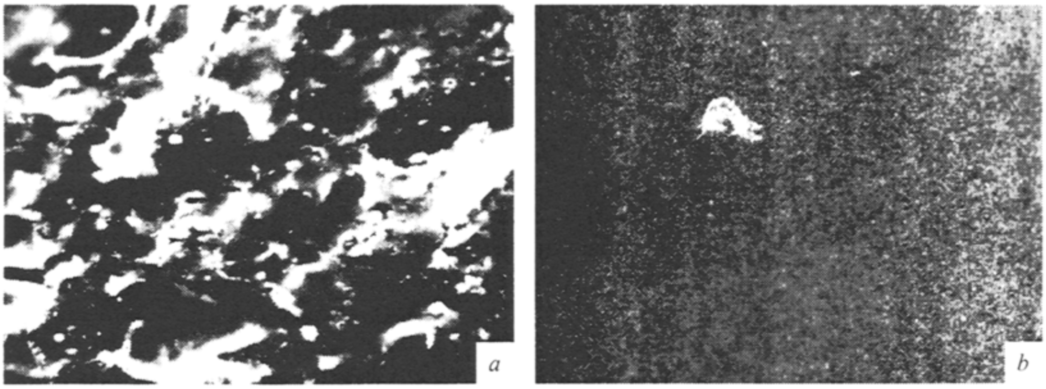

Fig. 4. Electron microscope photos of the surface of a photoglass ceramic samples before (*a*) and after (*b*) laser radiation (×1050).

state of matter. The sample heat-treated at 780°C shows a significantly decreased content of lithium disilicate and metasilicate. The crystal phase of β-eucryptite, which is higher-melting, predominates in the sample composition. Its melting point is 1388°C [4], whereas the meting points of lithium metasilicate and disilicate are 1202 and 1032°C, respectively.

As the result of laser radiation, the material is heated. Heat transfer in solid nonmetallic materials occurs mainly through lattice heat conduction. Two variants of the effect of radiation on the material surface are distinguished: heating of the solid phase and heating with a solid-liquid-vapor phase transformation. Two principally different mechanisms of the laser radiation effect on a material should be distinguished, depending on the density of the radiation flux directed to the surface. At low flux densities ($q < q_c$, where q_c is the flux critical density), the material layer which absorbs the radiation undergoes a phase transition at what is known as the vaporization temperature. As q increases, the level of q_c is attained when the material temperature is above the critical one, and in this case the phase transition is absent and the destruction of the material is observed. The radiation flux density at which the destruction of the material starts is expressed by the relationship [1]

$$q_c = \frac{\pi}{2}\sqrt{kC\rho\tau t_c}\,, \qquad (2)$$

where k is the thermal conductivity of the material; C and ρ are the heat capacity and density of the material; τ is the radiation pulse duration; t_c is the critical temperature, which is usually taken equal to the boiling temperature of the material;

The mechanism by which the lithium-aluminosilicate photoglass ceramic becomes amorphous under the effect of the laser radiation can be represented, in our opinion, in the following way. The crystal phases are melted due to the concentration of the radiant laser energy in the surface layer and the energy transfer through heat conduction to the bulk of the material. One should also take into account the effect of the nonlinear radiation absorption at the oscillatory levels of the Si – O – Si – R atomic groups. The fact is that the resonance absorption frequencies of the general unexcited state and the excited states of the Si – O – Si – R groups are virtually the same, if one neglects the anharmonic oscillations effect. It is known that the energy levels of a harmonic oscillator are equidistant.

The main absorption band in photosensitive lithium-aluminosilicate glasses and their crystallization products is located within the region of $8.1 - 10.7 \times 10^4$ Å [5], i.e., it relates to the laser radiation frequency of the oscillatory levels of CO_2 molecules in the LG-43 gas laser. However, areas of transparency to radiation are possible at wavelengths $10.2 - 11.2 \times 10^4$ Å. Taking into account the anharmonic phenomenon and, consequently, the energy levels being nonequidistant, the inhibition of the energy accumulation in the surface layer can be related to the fact that the absorption and radiation frequencies of the excited and standard states are different. As a consequence of the above processes, the heating and cooling of the material under the action of the laser beam proceeds at high rates. Accordingly, the resulting melt solidifies in the amorphous state. This reduces the crystal phase content.

The electron microscope photos of the surface of different fragments of photoglass ceramic samples after laser-beam treatment exhibit crystallized areas, amorphous areas, and areas of transition between the sample matrix and the site of laser beam action (Fig. 4).

The values of the tangent of the dielectric loss angle (Table 2) increase in samples undergoing laser treatment: in the photoglass ceramics heat-treated at temperature 780°C they range from 45×10^{-4} to 72×10^{-4} and in the samples heat-treated at temperature 250°C they range from 66×10^{-4} to 41×10^{-4}.

The described effect can be accounted for by the increased content of the amorphous phase and increase con-

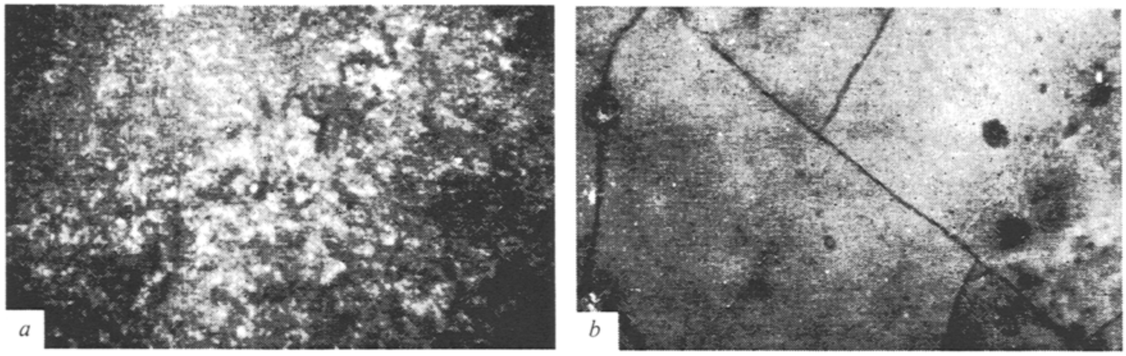

Fig. 5. Surface of a photoglass ceramic sample before (*a*) and after (*b*) laser radiation (×200).

centration of Li^+ and K^+ ions in the samples. As the crystal phases $Li_2O \cdot SiO_2$ and $Li_2O \cdot 2SiO_2$ melt, the Li^+ ions pass into the amorphous phase. Concentration of K^+ ions can take place due to the transition of the lithium metasilicate solid solutions formed in crystallization to the amorphous phase. The migration of these particles in the amorphous phase under the effect of thermal movement of ions along and against the field causes relaxation losses, increased dissipation of the electric field energy, and, accordingly, an increase in the tangent of the dielectric loss angle.

The study of the microhardness of the samples established the effect of a decrease in strength after laser radiation which decreases the sample microhardness (Table 2). The deterioration of strength properties of photoglass ceramics is related to the decrease in the crystal phase content and the increase in the amorphous phase content, which determines the strength of the material. Another reason are the thermal stresses that arise and, accordingly, the emergence of microcracks on the sample surface, which in certain cases join and lead to the emergence of macroscopic cracks and to brittle fracture of the material. The cause for the appearance of such cracks consists in the difference between the coefficient of thermal linear expansion (CTLE) of the crystalline and the amorphous phase. Thus, the CTLE of the initial lithium-aluminosilicate glass is $70 - 80 \times 10^{-7}\,°C^{-1}$, and the TCLE of the respective photo-sensitive glass ceramic is $100 - 120 \times 10^{-7}\,°C^{-1}$ [6].

This difference in the TCLE values of the glass and photoglass ceramic following laser treatment of the sample produces thermal stresses at the glass – glass ceramic boundary which are comparable to the ultimate strength of the material and which facilitate the emergence of microcracks. The emergence of microcracks on the surface of the photoglass ceramic was experimentally observed using an MIM-7 metallographic microscope, and it occurred in the amorphous phase. The microcracks had a random shape and were formed over the entire surface exposed to laser radiation (Fig. 5).

It is of interest that laser radiation also contributes to modification of the optical properties of the material. Some photoglass ceramic samples exhibited absolutely transparent sites which in their optical properties were similar to ordinary glass.

Thus, the effect of millisecond laser pulses with energy flux density ~ 1.6×10^2 W/cm^2 and wavelength 5008 Å on a glass ceramic cement significantly reduces the crystal phase content, renders the structure more amorphous, and decreases the microhardness.

Treatment of lithium-aluminosilicate photoglass ceramic by laser beams with energy flux 10^4 W/cm^2 and wavelength 10.6×10^4 Å renders its surface layer amorphous, increases the tangent of the dielectric loss angle, regularly decreases microhardness, and facilitates the formation of surface microcracks.

TABLE 2

Treatment temperature, °C	Samples before radiation			Samples after radiation		
	microhardness, GPa	tangent of dielectric loss angle, 10^4	volume concentration of the crystal phase, %	microhardness, GPa	tangent of dielectric loss angle, 10^4	volume concentration of the crystal phase, %
–	9.2	65	0	–	67	0
520	9.1	66	0	4.5	74	0
585	9.2	66	5 – 10	8.5	66	0
780	12.4	45	50 – 55	7.4	72	5 – 20

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